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THE EFFECT OF CERTAIN PIGMENTS ON LINSEED OIL; WITH A NOTE ON THE MANGANESE CONTENT OF RAW LINSEED OIL.

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At the time the Contracts Laboratory of the Bureau of Chemistry was making some exposure tests on painted steel plates some of the mixtures of various pigments of known composition with raw linseed oil of known analytical constants were set aside in closed jars of uniform shape and size in order to learn what changes would take place in the oil upon standing. No drier was added to these samples. The paints were so prepared that after the addition of drier they had approximately the same viscosity, 47 to 50 (water = 6.2), as determined by a Stormer viscosimeter. The jars were stoppered air-tight and placed in a closet having a glass door, where the light was dim and diffused.

The following table gives the list of pigments that were used and the proportions, by weight, of pigment and oil:

Table 1.—*Composition of paints.*

Pigment.	Pigment by weight.	Oil by weight.	Pigment.	Pigment by weight.	Oil by weight.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
White lead (basic carbonate)	72	28	Artificial graphite	42	58
Kaolin (contains $CaSO_4$)	50	50	Zinc white (American)	39	61
Indian red	50	50	Chrome yellow (lead chromate)	34	66
Flake graphite	40	60	Chromium oxid, green	51	49
Magnetic oxid, black[1]	46	54	Lampblack	16	84
Zinc yellow (zinc chromate)	45	55			

[1] Analysis by H. C. McNeil: Loss at 110° C., 0.56 per cent; Na_2CO_3, 2.82 per cent, $FeCO_3$, 18 per cent Fe_3O_4, 60.4 per cent; Fe_2O_3, 18.3 per cent.

At the end of one and two year periods the contents of each jar were well mixed and a portion poured out, thinned with ether, and centrifuged. After decanting the supernatant liquid from the pigment the greater part of the ether was evaporated on the steam bath, and the oil heated for half an hour at 105° C. in an inert gas, carbon dioxid being used for the one-year and hydrogen for the two-year samples. The last traces of pigment were removed by filtering through fine filter paper. The black pigments settled with difficulty. The oil extracted from the lampblack paint, was red and muddy and was not analyzed. Judging from its constants, appearance, and odor, the linseed oil purchased in the open market was undoubtedly unadulterated. The constants were as follows:[1]

Specific gravity (15.6° C.)	0. 934
Saponification number	193. 6
Acid number	1. 7
Iodin number	179. 6
Ash (per cent)	0. 13
Unsaponifiable matter (per cent)	0. 68

Unfortunately all the oil was used in making the paints, so that the changes which would occur in keeping it without pigments could not be noted. It has been proved, however, that raw linseed oil kept in glass away from bright sunlight for two years does not change appreciably with respect to its analytical constants, except for a slight rise in acid number.[2]

As the different pigments settled with different degrees of compactness in the jars, the surface of contact was larger in some cases than in others. Since the contents of the jars were mixed before sampling, the change in analytical figures as obtained represents an effect upon the total volume of oil. The results are shown in the following table:

TABLE 2.—*Effect of pigments on raw linseed oil.*

Pigment.	Time of exposure.	Specific gravity (15.6° C.).	Iodin number.	Ash.	Color.
	Years.			*Per cent.*	
White lead (basic carbonate)	1	0.940	175.8	0.35	Bleached.
	2	.938	177.3	.40	Do.
Kaolin	1	.939	173.0	.12	Very much bleached.
	2	.936	171.6	.14	
Indian red	1	.941	173.8	.15	Bleached.
	2	.939	172.5	.14	Do.
Flake graphite	1	.934	180.9	.21	Normal.
	2	.933	178.2	.15	Do.
Magnetic black	1	.937	174.6	.17	Do.
	2	.935	173.2	.13	Do.
Zinc yellow	1	.934	180.2	.20	Do.
	2	.934	179.5	.18	Do.
Artificial graphite	1	.935	181.0	....	Do.
	2	.939	180.8	.15	Do.
Zinc white	1	.935	181.3	.25	Do.
	2	.934	179.7	.13	Do.
Chrome yellow	1	.937	176.3	.14	Bleached.
	2	.935	175.7	.14	Do.
Chromium oxid, green	1	.937	178.0	.01	Do.
	2	.937	180.2	.05	Do.
Original oil	....	.934	179.6	.13	....

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[1] Analysis by E. M. Dawson.

[2] Proc. Amer. Soc. Test. Mat., 1911, *11*: 197.

Before commenting on the figures it may be well to discuss the general action of pigments on linseed oil. Toch[1] stated that the hydrolysis of the glycerids in linseed oil by moisture is hastened by the presence of lime or lead salts. White lead, sublimed lead, and zinc oxid all showed the same bleaching power within two weeks, irrespective of the kind of raw linseed oil used. Slow chemical reactions take place between the lead and zinc pigments and the oil. Painters sometimes prefer a white-lead paste which is old. Toch also stated that the iodin number of a pure raw linseed oil may be reduced to 110 by the addition of metallic salts, as Japan drier, but this statement does not mean that such a large reduction is caused by the reaction between pigment and oil.

Sabin[2] emphasized the strong action of litharge upon linseed oil and stated that the effect of red lead (Pb_3O_4) on oil may be due to the litharge content, as, by preparing a red lead from litharge in the form of an impalpable powder, thus securing practically complete oxidation to the higher oxids of lead, the product is without the usual action when mixed with oil. A mixture of white lead and oil dries more rapidly than oil alone, but so small is this increase that it is not recognized in practice. In the drying process the action of the inert pigments, asbestine, China clay, etc., is similar to that of white lead, which may be due to physical rather than chemical causes. In fact, no pigments are really inert to oil with respect to the drying process, and this pigment action is of great value in paint.

Klein[3] stated that linseed oil extracted from paint is frequently found to have a low iodin number and quoted Boettinger's[4] experiments which showed a reduction of the iodin number from 183.3 to 131 by white lead in 17 days, and to 122.2 in two months. Whiting and ocher showed the same changes. In the original article, however, Boettinger stated that the mixtures of oil and pigments were exposed to light and air, so that it was in reality a study of the effect of pigments on the amount of atmospheric oxidation of the oil.

Gardner[5] made mixtures of pigments and linseed oil, using very small quantities, and, after allowing them to stand, determined the increase in the amount of ash. Zinc oxid, white lead, and red lead were the only pigments that gave an appreciable increase in the amount of ash.

In a later paper[6] he gave the results of allowing linseed oil to stand in contact with different pigments for two years. Although the experiments were similar to those reported in this paper, the results were very different. The pigments that Gardner used were zinc oxid, basic carbonate of lead, combinations of lead and zinc pigments, barytes, silica, basic chromate of lead, red lead, iron oxid, carbon black, and graphite. The iodin number of the original oil was 181. The samples extracted from the pigments had iodin values varying from 135 to 163. The specific gravity was greatly raised by silica and iron oxid and slightly by most of the others. The pigments containing lead and zinc caused an increase in the amount of ash, showing actual chemical combination. Where the other constants were greatly changed the acid number of the oil was much raised. Gardner called attention to the fact that the combination of pigment and oil is due to hydrolysis with the formation of free fatty acid. The determination of this increase therefore is of importance as showing to what degree the glycerid has been broken up, thus increasing its tendency to combine with the pigment. In the case of the mixture of oil and silica hydrolysis took place, as shown by the high acid number, but the pigment did not go into solution. The viscosity of the mixtures, being slightly greater than that ordinarily found, is doubtless somewhat in excess of that of the paints listed in Table 1.

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[1] The Chemistry and Technology of Mixed Paints, 1907.

[2] Bottler and Sabin, German and American Varnish Making, 1912.

[3] Allen, Commercial Organic Analysis, 4th ed., 1910, *2*: 336.

[4] Chem. Ztg., 1898, *22*: 102, 558.

[5] Paint Technology and Tests, 1911.

[6] J. Franklin Inst., 1912, vol. 174.

As Gardner stated that in two of his jars a skin was formed upon the surface, it seems probable that air entered into the reaction. This may be the cause of the difference in the results. Again, if an oil containing certain metals in solution is heated in air to drive off the last traces of solvent, oxidation will occur in a short time.

The need of using an inert gas when heating oils extracted from paint is illustrated by the figures in Table 3. Oil A, extracted from a white-lead paste, contained some dissolved lead. The iodin number of the fatty acids was 185. Oil B was prepared by dissolving lead linoleate in pure raw linseed oil. The amount of lead in solution was 3.23 per cent, and the iodin number of the prepared oil was 177. Oil C was a pure raw linseed oil having an iodin number of 179. The oils were dissolved in ether, and, after distilling off the bulk of the ether, were heated at 98° to 99° C.

TABLE 3.—*Iodin numbers obtained by heating oil under different conditions.*

Oil.	Gas used.	Time of heating.	Iodin number.	Oil.	Gas used.	Time of heating.	Iodin number.
		Hours.				*Hours.*	
A	Air	2	173	C	Air	2	174
	Hydrogen	2	182		do	4	168
	Carbon dioxid	2	180		Hydrogen	2	177
B	Air	2	158		do	4	177
	do	4	143		Carbon dioxid	2	178
	Carbon dioxid	2	180		do	4	179
	do	4	174				

In order to have the iodin number furnish reliable information regarding the nature of the oil used in a paint, it is necessary to saponify and separate the fatty acids, making the determination on them. As the iodin number of the fatty acids is about 4 per cent greater than that of the glycerid, the lower limit for oil from North American seed is about 185 and from South American seed about 178.

Gardner stated that "when paints are stored for a considerable length of time and then examined for the iodin value of their oil content, a lowering of the iodin value should not constitute cause for rejection or be sufficient evidence that the oil was adulterated with oils of lower iodin value." This is still open to question, as the results of the work in the Contracts Laboratory indicate that but little change takes place during two years. The changes that occur in a closed paint can are naturally very different from those in a drying paint film. Although not yet shown to be true, it is probable that in the latter case under the influence of light, air, and moisture there is actually more chemical combination between pigment and oil. An oil showing a high acid number has more effect upon a pigment that is basic in its nature, such as white lead, than an oil with a very low acid number as that used for this work.

The results in Table 2 show that the iodin number is in no case reduced sufficiently to place it below a figure frequently given by samples of pure raw linseed oil. Since duplicate determinations of the iodin number often vary as much as two units, a difference not exceeding that must be disregarded in comparing the different samples. The lower limit for oil from North American seed is placed at 178,[1] from South American seed at 171.[2] In the Contracts Laboratory many samples from unknown sources, which have shown all the characteristics of pure raw oil, have had an iodin number of 170 to 172.

It is interesting to note that while the iodin number of the oil was changed only slightly in all the mixtures, a greater decrease was caused by so-called inert pigments, kaolin, and Indian red, than by the others which include the lead and zinc pigments.

The large amount of ash from the white-lead samples undoubtedly shows that some of the pigment has been actually dissolved by the oil. The other figures for ash, however, do not show with certainty that there has been an appreciable solution of pigment.

The specific gravity of the oil was raised slightly in almost every case, but as with the iodin number the effect of two years' exposure was practically the same as that of one year. The upper limit for raw oil is placed at 0.936 at 15.6° C.[1] Many of the extracted oils are slightly above that figure.

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[1] Proc. Amer. Soc. Test. Mat., 1909, *9:* 164.

[2] Proc. Amer. Soc. Test. Mat., 1911, *11:* 202.

A rise in specific gravity may be caused by the solution of some of the metallic portion of pigment in the oil, by volatilization of a portion of the oil, or by oxidation. Oxidation would be accelerated by small amounts of dissolved lead, manganese, or other catalytic agents. As the oil after two years showed no increase in specific gravity over the one-year figure (except in one case), the air inclosed in the jar probably had very little effect. The samples of extracted oil were rather small for an accurate specific-gravity determination, so that a difference of one or two units in the third decimal place must be disregarded.

Kaolin had greater bleaching effect than any of the other pigments, the black pigments and the zinc white causing practically no change in the color of the oil. The jars were filled completely, so that the influence of air must have been negligible for the first year. As a portion was removed at the end of that time, during the second year of exposure about 100 cc of air filled the space above the paint in the jar.

The constants of an oil mixed with a pigment into a thick paste might be changed more than those of oil in the kind of paint used in these experiments, for a greater proportion, if not practically all, of the oil would then be in direct contact with the pigment. Samples of oil extracted from stiff white-lead pastes in this laboratory have yielded fatty acids with an iodin number of 185. The nature and original constants of the oils were unknown. The addition of driers and thinners would also influence these constants, and the results of these experiments are comparable only with paints made exclusively of raw oil and pigment in such proportions that the paint is ready for use without thinning.

Although the effect of white lead upon the specific gravity and iodin number is, under these circumstances, practically no greater than that of some of the other pigments, it is evident from the amount of ash that a greater weight of the pigment has gone into solution; though, considering the higher atomic weight of lead, the extent of chemical action need be no greater. The lead chromate did not combine with the oil to so great an extent as the basic carbonate.

The tendency of some of the pigments is to increase slightly the specific gravity of the oil, in many cases raising it above the higher limit for pure raw linseed oil, 0.936; hence a figure obtained on the extracted oil which is near the lower limit for pure raw linseed oil, 0.932, may indicate the presence of other oils of lower specific gravity.

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[1] Proc. Amer. Soc. Test. Mat., 1909, *9:* 164.

NOTE ON THE MANGANESE CONTENT OF RAW LINSEED OIL.

In 1911 sixteen samples of raw linseed oil of known purity and source were sent out to the members of the Subcommittee on Linseed Oil of the American Society for Testing Materials. Voorhees[1] found manganese in the ash of all the samples. In the Contracts Laboratory the same oils were ashed and the amount of manganese determined. Thirty grams of oil were used and the manganese determined by the bismuthate method. Table 4 shows the results. The percentage of manganese is figured on the oil.

TABLE 4.—*Manganese content of raw linseed oil.*

Sample No.	Ash.	Manganese.	Sample No.	Ash.	Manganese.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
1	0.16	0.0004	9	0.19	0.0008
2	.02	.0005	10	.21	.0006
3	.03	Faint trace.	11	.05	Faint trace.
4	.16	.0005	12	.03	Faint trace.
5	.03	Faint trace.	13	.03	.0005
6	.18	.0003	14	.04	Faint trace.
7	.18	.0002	15	.16	.0005
8	.16	.0003	16	.16	.0003

Approved.

JAMES WILSON,
Secretary of Agriculture.

WASHINGTON, D. C., *December 4, 1912.*

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[1] Proc. Amer. Soc. Test. Mat., 1911, *11:* 209.

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